

Tidal salt marsh sediment in California, USA. Part 2: Occurrence and anthropogenic input of trace metals

Hyun-Min Hwang^{a,*}, Peter G. Green^{a,*}, Richard M. Higashi^{b,1}, Thomas M. Young^a

^a Department of Civil and Environmental Engineering, University of California, One Shields Avenue, Davis, CA 95616, United States

^b John Muir Institute for the Environment, Center for Health and the Environment, University of California, One Shields Avenue, Davis, CA 95616, United States

Received 9 September 2005; received in revised form 15 January 2006; accepted 17 January 2006

Available online 9 March 2006

Abstract

Surface sediment samples (0–5 cm) from 5 tidal salt marshes along the coast in California, USA were analyzed to investigate the occurrence and anthropogenic input of trace metals. Among study areas, Stege Marsh located in the central San Francisco Bay was the most contaminated marsh. Concentrations of metals in Stege Marsh sediments were higher than San Francisco Bay ambient levels. Zinc (55.3–744 $\mu\text{g g}^{-1}$) was the most abundant trace metal and was followed by lead (26.6–273 $\mu\text{g g}^{-1}$). Aluminum normalized enrichment factors revealed that lead was the most anthropogenically impacted metal in all marshes. Enrichment factors of lead in Stege Marsh ranged from 8 to 49 (median = 16). Sediments from reference marshes also had high enrichment factors (2–8) for lead, indicating that lead contamination is ubiquitous, possibly due to continuous input from atmospherically transported lead that was previously used as a gasoline additive. Copper, silver, and zinc in Stege Marsh were also enriched by anthropogenic input. Though nickel concentrations in Stege Marsh and reference marshes exceeded sediment quality guidelines, enrichment factors indicated nickel from anthropogenic input was negligible. Presence of nickel-rich source rock such as serpentinite in the San Francisco Bay watershed can explain high levels of nickel in this area. Coefficients of variation were significantly different between anthropogenically impacted and non-impacted metals and might be used as a less conservative indicator for anthropogenic input of metals when enrichment factors are not available.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Tidal salt marsh; Sediment; Trace metal; Anthropogenic input; Enrichment factor

1. Introduction

After many regulations, especially the Clean Water Act, environmental metal inputs from mining and other point sources such as metal processing facilities have been significantly reduced. As a result, in San Francisco Bay (SFB), the total metal load from wastewater discharge declined from 993 t yr⁻¹ in 1960 to 171 t yr⁻¹ in 1986 and to 46 t yr⁻¹ in 1999 (Monroe and Kelly, 1992; Squire et al., 2002). Total

annual loadings of lead from publicly owned treatment works (POTWs) significantly declined from 2.29 t yr⁻¹ in 1989 to 0.7 t yr⁻¹ in 1999. During the same period silver loading from POTWs declined from 1.7 t yr⁻¹ in 1989 to 0.65 t yr⁻¹ in 1999 (Squire et al., 2002). However, metals from non-point sources are increasing due to the growth of population in urban areas. The quantity of Zn released by tire wear has been increasing and in the mid-1990s, it was comparable to that released from waste incineration in the US (Councell et al., 2004). Urbanization with population growth showed a strong positive correlation with increased traffic activity (SFEI, 2005a), which is responsible for much of the contamination of traffic related elements (e.g., Cu, Pb, Zn) in urban areas (Callender and Rice, 2000; Councell et al., 2004). For example, approximately 63% and

* Corresponding authors. Tel.: +1 530 752 8581; fax: +1 530 752 7872.
E-mail addresses: hmlhwang@ucdavis.edu (H.-M. Hwang), pggreen@ucdavis.edu (P.G. Green).

¹ Present address: Center for Regulatory and Environmental Analytical Metabolomics, Department of Chemistry, University of Louisville, Louisville, KY 40292, United States.

24% of the total annual load of lead entering into SFB is delivered through urban runoff and fluvial input, respectively (Squire et al., 2002). Rice et al. (2002) showed that stormwater runoff is a significant source (up to 90% of the total) of sedimentary copper in a suburban lake in densely populated northern Virginia. A study on sources and sinks of zinc in urban–suburban watershed in the Washington, DC, metropolitan area showed that tire-wear zinc inputs can be significantly greater than atmospheric inputs (Counsell et al., 2004). Consequently, the quality of many urban rivers, lakes, estuaries, and coastal oceans has not recovered yet to the safe level for protection of human health and natural resources.

Due to very low solubility in water with a neutral or basic pH and particle-reactive behavior, metals in the water column tend to be adsorbed on solids that settle (Fostner and Wittman, 1983). Consequently, sediments are recognized as the final repository for a substantial fraction of the metal load in many watersheds and can therefore provide a long-term integrated source of information regarding environmental quality. Unlike organic contaminants (e.g., DDTs, PCBs), metals are not biologically or chemically degraded so sediment bound metals are likely to persist much longer in the environment. Thus, metals can affect the health of wildlife and humans long after their major sources have been removed. A good example is the bay-wide high level of mercury originating mainly from previous mining activities (Alpers and Hunerlach, 2000; SFEI, 2005b). Though mercury loading from mercury and gold mining into SFB was significantly reduced in the early 20th century (Nriagu, 1994), mercury in SFB is still threatening human health and it appears likely that these health effects will continue into the future due to resuspension of sediment contaminated by historic activities and, by contemporary inputs from other industrial activities (Flegal et al., 2005; Greenfield et al., 2005). The fish consumption advisory for mercury in SFB was issued in December 1994 and is still effective (OEHHA, 1999). Greenfield et al. (2005) found no apparent increasing or decreasing trends of the mercury concentrations in striped bass from the early 1970s to the late 1990s.

Tidal marshes serve many important environmental functions. Among the components of tidal salt marshes, marsh plants play many beneficiary roles in supporting and sustaining the health and diversity of the marsh ecosystem (Mitsch and Gosselink, 2000). Stands of marsh plants can serve as a nursery area for estuarine fish and shellfish (Sogard and Able, 1991). Marsh plants are also an important source of food for waterfowl and wetland mammals (Goals Project, 2000). However, this fact can threaten the health of marsh plant eating animals especially in contaminated marshes such as Stege Marsh (ST). Marsh plants can accumulate metals in their roots, stems, and leaves (Weis and Weis, 2004) and consequently can transport sedimentary metals to animals feeding on marsh plants, resulting in enhanced biomagnification of metals in these animals. In SFB, a vast majority (~80%) of wetland area has disap-

peared during the last 150 years and the remaining wetlands are fragmented resulting in a correspondingly fragmented distribution of certain wildlife (Goals Project, 1999). When these fragmented wetlands are also stressed by heavy contamination with multiple toxic chemicals, as in the case of ST, populations of wetland dwelling animals such as the endangered clapper rail and vegetarian mice and voles may be greatly diminished soon in the worst case. It is therefore important to quantify the degree of contamination and its impact on the health of wetland ecosystem.

Sediment samples from 5 tidal marshes along the coast of California were analyzed for trace metals to establish current metal distributions within the marshes, the degree to which sedimentary metals resulted from anthropogenic inputs, and to investigate the relationship of inputs to surrounding land use patterns. Organic contaminant concentrations were also measured on the same set of samples and were reported in a previous paper (Hwang et al., *in press*). Chemical analysis data obtained from the current study will also support subsequent validation of biological indicators of ecosystem health and identification of chemicals responsible for toxic effects in aquatic organisms. The combination of rich chemical and biological datasets is essential to develop appropriate management strategies for these complex ecosystems.

2. Methods and study areas

Details about sampling areas and sample collection are described in a previous paper (Hwang et al., *in press*). Sampling locations, surrounding land use patterns, and possible major sources of metals are presented in Table 1. Surface (0–5 cm) sediment samples were collected using a Teflon piston pipe in June 2003 from 5 marshes (Stege Marsh (ST), China Camp (CC), Tom's Point (TP), Walker Creek (WC), Carpinteria Marsh (CS)) in 3 different coastal regions of California. Sampling areas are shown in Fig. 1. Study areas were selected to compare impacts of trace metals in tidal salt marsh sediments from highly urbanized (ST), moderately urbanized (CS), and remote areas (CC, TP, WC). In ST and CS, sediment samples were collected at 13 and 12 stations, respectively, allowing a more comprehensive assessment of spatial metals distribution. Sediment samples for metal analysis were stored in glass jars and kept frozen (–20 °C) until analysis was performed.

Sediment metal concentrations were determined using the method of Higashi et al. (2005). Metals analyzed for this study include aluminum (Al), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), lithium (Li), nickel (Ni), silver (Ag), vanadium (V), and zinc (Zn). Mercury (Hg) was not analyzed for this study. To measure near-total metals, an aliquot (~500 mg) of wet sediment and 2 ml of concentrated trace metal grade HClO₄ (70%) and HNO₃ (65%) mixture (1:5) were added into a tall glass tube. Each batch of samples (~20 samples)

Table 1
Locations and land use patterns of study areas

Study area	No. of stations	Collection elevations	Location	Land use	Possible major anthropogenic sources of metals
Stege Marsh	12	Marsh edge, creek bank	San Francisco Bay, Northern California	Urban/Industrial	Previous industrial and agricultural chemical manufacturer, Previous city landfill, Stormwater runoff
China Camp	3	Marsh edge, creek bank	San Francisco Bay, Northern California	Rural/State Park	Previous shrimping village
Tom's Point	3	Marsh edge, creek bank	Tomales Bay, Northern California	Rural	No known sources
Walker Creek	3	Marsh edge, creek bank	Tomales Bay, Northern California	Rural	Mercury mine
Carpinteria Marsh	13	Marsh edge, creek bank, creek bottom	Southern California	Suburban/Agricultural	Stormwater runoff, Greenhouses

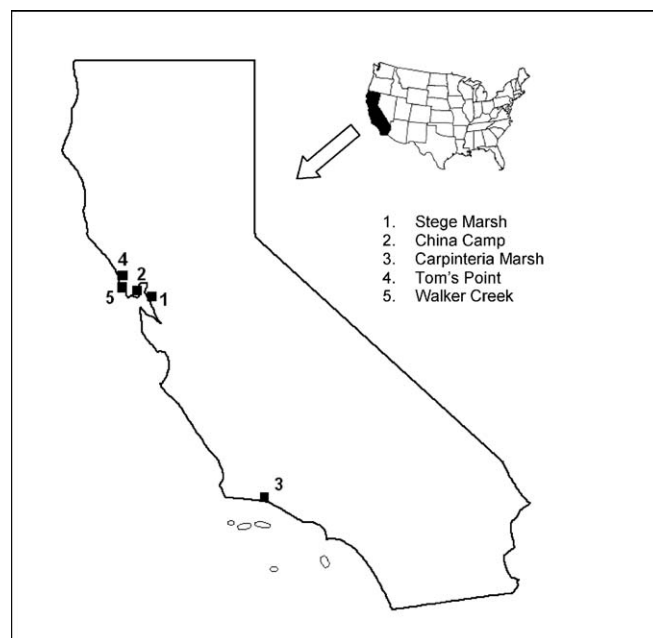


Fig. 1. Map showing the study areas.

included one procedural blank, sample duplicate, matrix spike, and standard reference material (NIST 1646a) to validate quantification data. Tubes were kept at room temperature overnight and then were placed in the digestion block. The temperature of the digestion block was increased to 200 °C in several steps over 4 h to enhance digestion. Tubes were then centrifuged at 2000 rpm for 10 min. An aliquot (1 ml) of extract was removed from the tubes and diluted 500 times for instrumental analysis. Quantification of metals was performed using an Agilent 7500i argon plasma ICP–MS (Inductively Coupled Plasma–Mass Spectrometer, Palo Alto, CA). Concentrations in blanks were not compensated. Relative percent differences for duplicate samples were within 25%. The levels of target compounds in SRMs were within 30% of certified values except for Al, Cr, and V, which are known to be incompletely recovered using out digestion method (Cook et al., 1997; Hornberger et al., 1999). In order to obtain dry weight, wet sediment samples (~1 g) were dried at 60 °C for 24 h. Chemical concentrations are reported on a dry weight basis.

3. Results and discussion

Concentrations of metals in sediments from 5 tidal salt marshes in California are given in Table 2, which summarizes data from all stations and all elevations (marsh edge, creek bank, creek bottom). As in the case of organic contaminants, such as PAHs, PCBs, and chlorinated pesticides (Hwang et al., in press), ST had much higher levels of metals compared to other marshes as well as ambient SFB surface sediment. Ambient SFB metal concentrations were estimated by the 85th percentile concentrations in surface sediments collected from the cleanest

Table 2
Concentrations ($\mu\text{g g}^{-1}$) of metals in sediments from tidal salt marshes in California

	Range	Median	Mean	SD ^a	CV ^b	Range	Median	Mean	SD ^a	CV ^b
	<i>Aluminum (Al)^c</i>					<i>Iron (Fe)^c</i>				
ST	1.96–5.27	2.93	3.15	0.82	26	2.47–6.88	4.11	4.05	1.02	25
CS	0.19–3.90	0.63	1.37	1.15	84	0.35–4.69	0.92	1.72	1.03	76
CC	1.90–5.97	2.99	3.55	1.21	34	3.34–7.44	3.57	4.26	1.60	37
TP	1.81–4.28	2.38	2.78	1.09	39	1.79–4.83	2.40	2.81	1.21	43
WC	1.38–4.45	2.37	2.76	1.14	41	1.76–4.99	3.43	3.50	1.17	33
	<i>Arsenic (As)</i>					<i>Cadmium (Cd)</i>				
ST	6.08–40.8	12.9	15.9	8.6	54	0.11–1.67	0.35	0.46	0.34	75
CS	1.79–13.3	3.24	5.10	2.97	58	0.04–0.81	0.15	0.23	0.15	63
CC	4.86–19.3	13.6	12.3	5.6	46	0.10–0.38	0.27	0.24	0.11	46
TP	3.72–11.0	6.50	7.37	3.02	41	0.05–0.28	0.18	0.18	0.10	54
WC	6.00–15.0	10.0	9.74	3.37	35	0.15–0.27	0.20	0.21	0.05	22
	<i>Chromium (Cr)</i>					<i>Copper (Cu)</i>				
ST	32.5–100	13.1	53.9	14.6	27	24.8–189	67.9	78.3	46.6	59
CS	3.70–35.5	52.5	18.3	9.5	52	1.68–67.5	5.24	15.1	17.3	115
CC	34.0–104	74.8	70.3	29.0	41	20.0–94.6	54.5	51.3	26.4	51
TP	30.0–64.0	42.2	44.6	14.3	32	7.14–36.0	14.9	19.2	11.4	59
WC	48.1–83.3	52.4	59.1	14.3	24	14.3–42.1	23.9	25.6	11.1	43
	<i>Lead (Pb)</i>					<i>Lithium (Li)</i>				
ST	26.6–273	64.6	87.9	59.7	68	20.1–45.1	26.9	28.8	6.6	23
CS	1.56–101	4.26	6.78	3.83	56	1.69–29.6	7.20	12.4	8.4	68
CC	14.6–19.3	16.5	16.8	2.0	12	28.9–61.2	56.2	52.3	18.5	35
TP	4.83–16.8	8.02	56.4	24.2	43	15.5–32.0	20.1	22.2	7.0	31
WC	8.03–19.3	12.6	27.7	5.2	19	20.5–49.1	30.9	31.7	10.0	31
	<i>Nickel (Ni)</i>					<i>Silver (Ag)</i>				
ST	31.0–84.6	49.5	51.1	12.6	25	0.13–0.65	0.23	0.28	0.12	43
CS	3.39–57.7	10.1	20.3	15.6	77	0.02–3.27	0.05	0.24	0.57	240
CC	34.3–94.8	89.9	75.1	27.7	37	0.11–0.49	0.40	0.33	0.16	49
TP	30.0–78.8	41.8	48.8	19.9	41	0.03–0.06	0.04	0.04	0.01	28
WC	48.5–94.4	75.1	71.6	17.7	25	0.04–0.11	0.06	0.07	0.03	40
	<i>Vanadium (V)</i>					<i>Zinc (Zn)</i>				
ST	30.1–77.8	44.2	46.9	11.5	25	55.3–744	201	273	210	77
CS	4.08–62.3	13.4	23.0	16.5	72	7.41–510	24.6	81.5	108	133
CC	35.8–92.9	86.5	73.3	25.6	35	40.5–253	103	109	76	69
TP	23.9–61.7	34.7	40.0	15.9	40	23.7–123	55.9	67.2	35.6	53
WC	33.4–73.7	47.1	49.9	16.6	33	31.2–134	54.5	68.1	40.1	59

ST (Steger Marsh), CS (Carpinteria Marsh), CC (China Camp), TP (Tom's Point), WC (Walker Creek).

^a Standard deviation.

^b Coefficient of variation (percentage of SD against mean).

^c Concentration unit of Al and Fe is %.

portion of SFB using data from the Regional Monitoring Program (RMP) and the Bay Protection and Toxic Cleanup Program (SFBRWQCB, 1998). Ambient concentrations of some metals such as Ag, Cu, Pb, and Zn are still higher than pre-World War II regional background levels (Hornberger et al., 1999) due to continuous input from point and non-point sources, bioturbation, and sediment resuspension. As discussed below, anthropogenic enrichment factors of metals, especially lead, zinc, copper, and silver, indicate that ST has been severely influenced by human activities. Many metals in ST exceeded sediment quality guidelines (Hwang et al., submitted for publication-a) so sediments in ST have high potential to cause adverse biological effects. TP and WC had very low levels of metals and can be regarded as reference marshes. In CS, median concentrations of the most anthropogenically

impacted metals (copper, lead, and zinc) were generally lower than the lowest concentrations found at the reference sites indicating that overall sediment quality in CS is relatively good. Although Table 2 pools data from all elevations, there were some systematic differences in metal concentrations with elevation (data not shown). Creek bank sediments in ST had higher levels of metals compared to marsh edge sediments, especially for copper, lead, and zinc. For example, lead in creek bank and marsh edge sediments ranged from 37 to 272 $\mu\text{g g}^{-1}$ and 26.6 to 117 $\mu\text{g g}^{-1}$, respectively.

To assess spatial distribution patterns, concentrations of Cu, Zn and Pb in creek bank sediments are presented along transects from upstream to downstream stations of the main channels in ST and CS (Fig. 2). This comparison was restricted to creek bank sediments because they are less

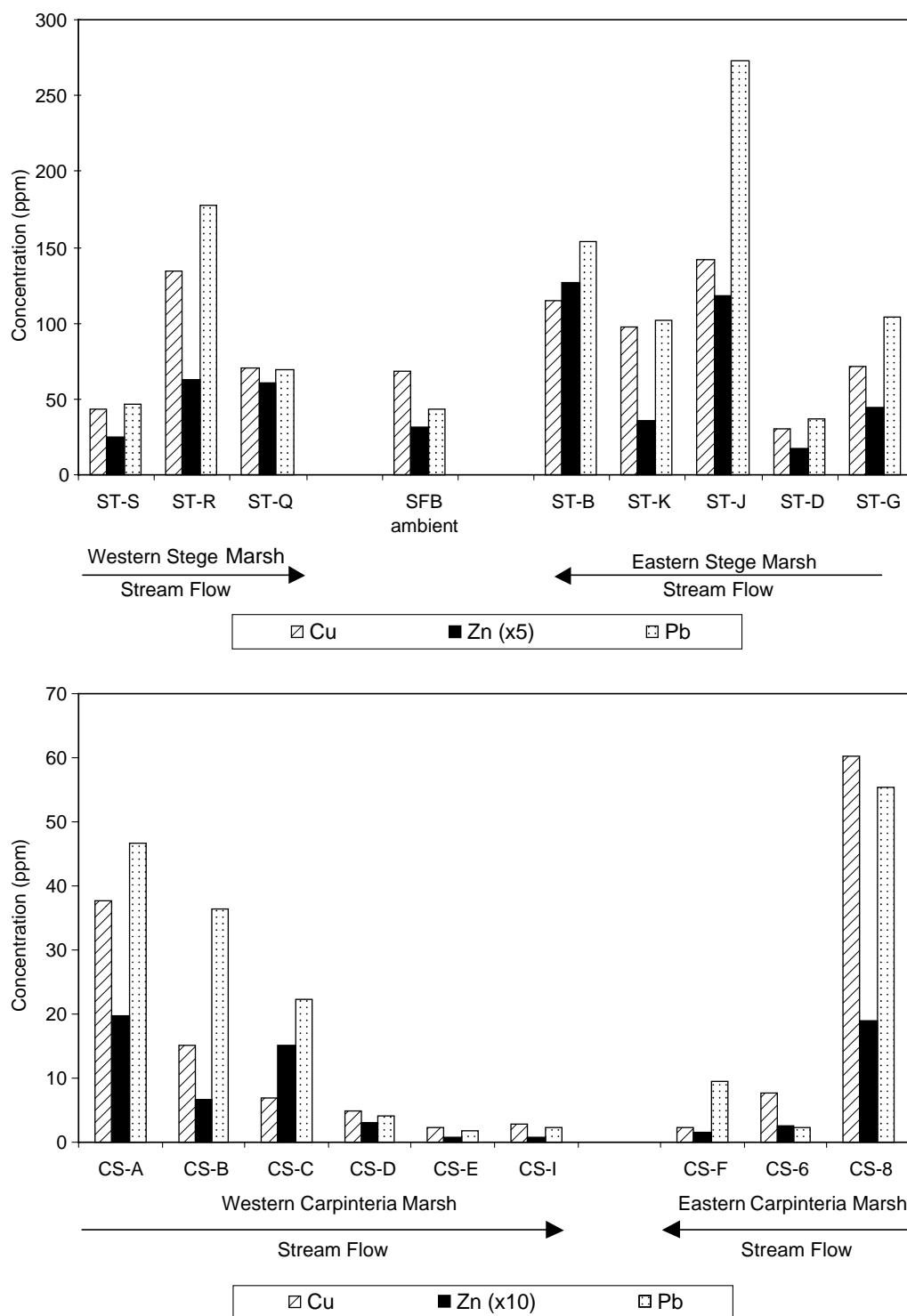


Fig. 2. Spatial distribution of metals in sediments from Stege Marsh (ST) and Carpinteria Marsh (CS), California.

likely to be affected by marsh plants than marsh edge sediments and because creek bottom sediments were only collected from CS. Within each marsh, most metals exhibited a similar spatial distribution pattern to each other and to that observed for organochlorine compounds (Hwang et al., in press), indicating that contaminant source areas

are probably similar and that tidal action plays an important role in transporting particle-bound organic contaminants and metals. In CS metal concentrations generally decline with travel distance from the head of the marsh while in ST the metal spatial distribution was more heterogeneous, showing no systematic increase or decrease with

distance from the head of the marsh. Possible reasons for these differing patterns are discussed below.

One potential explanation for the spatial variability in metal concentrations is heterogeneous distribution of organic matter in the sediments. Metals are readily adsorbed onto organic materials and fine particles such as silt and clay, so lateral and vertical distribution of metals can be influenced by these parameters (Fostner and Wittman, 1983). In order to assess the impact of these parameters on the metal distribution in ST, concentrations of metals were compared with the amount of organic carbon (Kuivila, unpublished) and fine sediments (Grosholz, unpublished). Neither parameter showed good correlation with metal concentrations. Regression coefficients (r) of both metal–organic carbon content and metal–fine sediment fraction relationships were much lower than 0.5, so they cannot explain the heterogeneous spatial distribution and difference between creek bank and marsh edge sediments. Complex sources and/or physical alteration by previous remediation and construction activities might be possible explanations for the metal distribution in ST. In western ST, most metals exhibited higher concentrations at ST-R compared to upstream (ST-S) and downstream (ST-Q) stations. Again, this difference is not related to the fraction of organic carbon and fine sediment. So there seems to be an additional input of contaminants between ST-R and ST-S. Between these two stations, there is a small creek that starts from the location of a former industrial and agricultural chemical manufacturing company. Due to high levels of contaminants, remediation is ongoing in this area, including station R. In CS, metal concentrations were always the highest at the most upstream stations (CS-A and CS-8) and decreased rapidly with increasing distance from the head of the creek. The most downstream station (CS-I) exhibited the lowest concentrations of all metals throughout the present study. Contrary to ST, marsh edge sediments at some stations had higher levels of metals compared to creek bank sediments. Overall spatial concentration variation was much greater in CS, which may be due to the longer distance between the most upstream stations that are close to sources and the most downstream stations that meet with coastal ocean. In ST, contaminated waters from upstream are diluted by relatively contaminated SFB water, while CS is diluted directly by coastal ocean water, which is cleaner. For the present study, bulk sediment samples were digested with a mixture of concentrated acids (HClO_4 and HNO_3). It is generally known that digestion with concentrated acids can provide near-total metal concentrations that are much higher than those obtained using dilute acid digestion (e.g., 0.5 N HNO_3), which is likely to extract only the readily bioavailable fraction (Peijnenburg and Jager, 2003). However, concentrated nitric acid digestion is not strong enough to dissolve some metals (e.g., Al, Cd, Cr, V) completely compared to digestion with hydrofluoric acid, which can provide total decomposition of sediments (Cook et al., 1997; Hornberger et al., 1999). Therefore, comparison of data from this study with data

from other studies that used different acids (e.g., dilute acid, strong acid, hydrofluoric acid) requires caution. Especially when aluminum (Al) is used as a normalization element to calculate metal enrichment factors, the dissolving power of the digestion acid for background and samples must be similar, otherwise the contribution of anthropogenically originated metal can be significantly underestimated or overestimated depending on the type and concentration of acid that is used for extraction.

Sedimentary metal data reported by SFBRWQCB (1998) and Hornberger et al. (1999) were used to provide reference concentrations for northern California marshes (ST, CC, TP, WC). These studies used concentrated nitric acid digestion to dissolve sedimentary metals so no adjustment was made to compare data from these studies with that from the present study. For the southern California marsh (CS), metal concentrations were compared with data reported by Schiff and Weisberg (1999). Because Schiff and Weisberg (1999) used diluted acids (0.1 N of nitric acid and 1.0 N of hydrochloric acid) for digestion, some metals may exhibit much lower concentrations than actual concentrations. Reference data reported by SFBRWQCB (1998), Hornberger et al. (1999) and Schiff and Weisberg (1999) are presented in Table 3.

Lead concentrations in ST sediments were much higher than in the other marshes. Sedimentary lead concentrations in 10 out of 13 creek bank samples from ST were higher than the SFB ambient sediment level ($43.2 \mu\text{g g}^{-1}$). Because there are no known current major point sources of lead in ST, historic point and non-point sources may be the major sources of lead. A spill at a lead battery manufacturer located upstream of Carson Creek may have been responsible for significant lead addition to ST sediments. During

Table 3
Regional background and ambient sedimentary metal concentrations ($\mu\text{g g}^{-1}$) in San Francisco Bay and Southern California Bight

	Hornberger et al. (1999)	SFBRWQCB (1998)	Schiff and Weisberg (1999)
Al ^a	3.7	NA	1.05
Fe ^a	3.7	NA	1.86
As	NA	15.3	5.0
Cd	NA	0.33	0.19
Cr	123	112	31
Cu	25	68.1	12
Pb	5	43.2	8.9
Ni	116	112	18.0
Ag	0.1	0.58	0.13
Zn	75	158	57

Hornberger et al. (1999): Pre-World War II regional background levels in sediment core samples collected from the central San Francisco Bay.

SFBRWQCB (1998): Ambient concentrations (85th percentile of the concentrations in surface sediments collected from the cleanest portion of San Francisco Bay).

Schiff and Weisberg (1999): Background concentrations in Southern California sediments that were obtained using metal–iron baseline relationships.

NA: Not available.

^a Concentration unit of Al and Fe is %.

the 1940s through the 1960s, ST was used as a city landfill and substantial quantities of lead-containing crushed battery casings were deposited (URS, 1999). Stormwater runoff also delivers a considerable amount of lead (Squire et al., 2002). According to Dunlap et al. (2000), anthropogenic input of lead from past leaded gasoline emissions still accounts for more than 50% of the total lead load into SFB from the Sacramento and San Joaquin Rivers. Using lead isotope analysis, Steding et al. (2000) showed that lead from past leaded gasoline emission persists for decades in the SFB estuary system. In the southern reach of SFB, lead from these past emissions, which occurred in the 1960s through 1970s, still accounted for about 90% of total lead in water samples collected in 1998. So, a considerable portion of lead in ST also originated from previous use of leaded gasoline. Sedimentary lead in CS exhibited a wide range of concentrations. The median concentration was lower than the lowest concentration found in reference marshes. High lead concentrations were found only at a few of the most upstream stations. Stormwater runoff from urban areas and highways may be the major input pathway at these locations.

At all of the study areas, zinc was the trace metal that was detected at the highest concentration. Zinc in 11 out of 13 creek bank sediments in ST was higher than that in SFB ambient sediment ($170 \mu\text{g g}^{-1}$). The highest concentration of Zn was found at station P, which is the closest station to the former chemical manufacturing facility. As and Cu also exhibited the highest concentrations at this station. All of the sediment samples from CC, TP, and WC (except CC-A) had lower levels of Zn compared to SFB ambient sediment. The major anthropogenic sources of Zn are metal production, waste incineration, vehicle operation, fossil fuel consumption, and phosphate fertilizer (Makepeace et al., 1995; Councell et al., 2004). Urban and highway runoff has a considerable amount of tire wear particles and brake pad wear particles (Makepeace et al., 1995; Caltrans, 2003) and contributes to elevated levels of Zn and Cu in receiving watersheds (Rice et al., 2002; Bay et al., 2003). Tires and brake pads are well known sources of Zn and Cu (Davis et al., 2001). Tire-tread material contains Zn about 1% by weight (Councell et al., 2004). Copper in more than 50% of sediment samples from ST exceeded SFB ambient sediment levels ($68.1 \mu\text{g g}^{-1}$). Releases from the former chemical manufacturing facility and inputs from stormwater runoff may be the most important sources of Cu in ST. All CS samples contained lower levels of Cu than SFB ambient sediment. There are no known point sources that discharge contaminants directly into CS. So stormwater runoff might be the major source of Cu and Zn in CS.

Unlike other metals such as Pb and Zn, concentrations of Ni in ST were not higher than reference marshes (Table 2). CC and WC had higher levels of Ni than ST. This suggests that perhaps Ni from natural source is predominant in ST and therefore anthropogenic input of Ni may not be important. As discussed below, enrichment factors confirm that Ni is one of the least anthropogenically impacted

metals in all study areas. Compared to northern California marshes, the southern California marsh CS had much less Ni. This might be due to the mineralogical difference between southern and northern California. Schiff and Weisberg (1999) found a latitudinal gradient of regional variability in sedimentary Ni concentrations within the Southern California Bight. Nickel concentrations increased toward the north due to naturally high Ni in the source rocks north of the Southern California Bight. In the present study, a geographical mineralogical difference was also found for other metals such as Al, Fe, and Cr. Median concentrations of Al (0.63%), Fe (0.92%), and Cr ($13.1 \mu\text{g g}^{-1}$) in CS were much lower compared to northern California reference marshes (Table 2). Naturally weathered soils in southern California contain lower levels of some metals compared to northern California.

Metal data were subjected to linear regression analysis to identify any correlations among metals measured in the present study. Regression was performed for samples from ST and CS separately (Table 4). Several factors, such as sources, sediment grain size, organic carbon content, partition coefficients, and redox condition, can affect the variation of metals in sediment. Variable digestion efficiency may also affect the correlation of metals. The mean regression coefficient of all metal–metal relationships in CS sediments (0.76; SD = 0.19) is higher ($p < 0.001$) compared to that in ST sediments (0.52; SD = 0.24), providing additional evidence that metal distribution in ST is very heterogeneous. Regression coefficients of metal–Al and metal–Fe relationships in ST sediments cannot differentiate anthropogenically contaminated and uncontaminated metals. Though anthropogenic enrichment of Ni is negligible (see below), regression coefficients of Ni–Fe and Ni–Al relationships in ST sediments are very low. In CS, Al and Fe can account for the variation of all metals (except Ag). Regression coefficients of As, Cr, Ni, and V with Al and Fe are 0.89 or higher, indicating these metals are unlikely to have been significantly impacted by human activities. Anthropogenically impacted metals such as Cd, Cu, Pb, and Zn also generally have relatively higher regression coefficients (0.71 or higher) with Fe and Al. In both marshes, copper and zinc correlated to each other significantly ($r \geq 0.95$). This suggests that sources, transport mechanisms, and geochemical fate of these two metals are very similar. In CS, regression coefficients of all metal–Al relationships are almost identical to those of metal–Fe relationships. Though slightly more variable, a similar pattern is also found in ST, indicating that Al or Fe can be used as reference elements in CS and ST. However, as described below, the digestion method needs to be considered to choose an appropriate reference element.

3.1. Enrichment factors

In order to enhance environmental quality, contaminant loads from various sources need to be reduced. This goal can be achieved more efficiently with less cost by adopting

Table 4

Regression coefficients (*r*) of metal–metal relationships in sediments collected from Stege Marsh (ST) and Carpinteria Marsh (CS), California

	Ag	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	V	Zn
<i>ST</i>											
Ag	1.00										
Al	0.10	1.00									
As	0.44	0.59	1.00								
Cd	0.84	0.10	0.41	1.00							
Cr	0.81	0.10	0.28	0.42	1.00						
Cu	0.52	0.73	0.86	0.61	0.22	1.00					
Fe	0.10	0.82	0.69	0.14	0.10	0.69	1.00				
Ni	0.75	0.37	0.59	0.47	0.84	0.59	0.31	1.00			
Pb	0.65	0.43	0.45	0.75	0.34	0.76	0.30	0.55	1.00		
V	0.41	0.63	0.76	0.14	0.58	0.66	0.56	0.84	0.37	1.00	
Zn	0.39	0.74	0.77	0.52	0.12	0.95	0.61	0.51	0.77	0.59	1.00
<i>CS</i>											
Ag	1.00										
Al	0.35	1.00									
As	0.48	0.92	1.00								
Cd	0.46	0.75	0.81	1.00							
Cr	0.32	0.89	0.89	0.75	1.00						
Cu	0.68	0.85	0.88	0.88	0.77	1.00					
Fe	0.33	0.98	0.91	0.71	0.89	0.82	1.00				
Ni	0.24	0.96	0.91	0.79	0.94	0.81	0.95	1.00			
Pb	0.39	0.75	0.71	0.88	0.68	0.88	0.73	0.77	1.00		
V	0.45	0.97	0.97	0.80	0.92	0.88	0.95	0.95	0.73	1.00	
Zn	0.79	0.75	0.77	0.81	0.63	0.96	0.71	0.66	0.83	0.77	1.00

appropriate management activities. To develop effective management strategies, fundamental information such as the sources of numerous contaminants must be identified accurately. Contrary to organic contaminants such as PCBs and chlorinated pesticides, which have only anthropogenic origins, trace metals can come from both anthropogenic and natural sources. Metals are introduced into aquatic systems as a result of weathering of soils and rocks as well as from a variety of human activities involving the mining, the processing or the use of metals. The natural occurrence of metals in the soil and sediment as well as geographical mineralogical variation can hamper the accurate assessment of anthropogenic input of metals. Generally, the anthropogenic contribution of metals can be identified by comparing metals in environmental samples to a representative background, which is obtained from regional soil data or sediment core data. To minimize the effects of geographical variations and sediment grain size, concentrations of each metal in samples and background are normalized with reference elements such as Al and Fe that are major components of sediment and are less affected by anthropogenic sources. Then, anthropogenic input of metals can be suspected when normalized concentrations of metals in samples are higher than background levels.

Among parameters (e.g., Fe, Al, Li, grain size, organic carbon) that can be used for normalization, Fe and Al have been used most frequently (Daskalakis and O'Connor, 1995). The normalization parameter needs to be selected carefully due to certain conditions. Aluminum has a limitation as a reference element when samples are digested with acids other than hydrofluoric acid. It has been reported

that the recovery of Al is low and variable when other acids are used for sample digestion. Schiff and Weisberg (1999) found much higher recovery for Fe (80%) than for Al (20%) with diluted nitric acid digestion. Hornberger et al. (1999) also obtained the same results showing recovery for Al (43%) was not as high as that of Fe (78%) when concentrated nitric acid was used to digest reference materials. Recoveries for both Fe and Al were the same (92%) when hydrofluoric acid digestion was applied. The less efficient dissolving capacity of other acids can cause variability in the recovery of Al, depending on samples, and may produce greater uncertainties for enrichment factors when data are compared to metal concentrations obtained by hydrofluoric acid digestion.

Under certain conditions, Fe also has a limitation as a reference element. Greater reduction potential of Fe in anaerobic sediments can enhance mobilization of more water soluble reduced Fe in pore waters (Luoma, 1990). When Fe is exposed to aerobic conditions, it is oxidized and forms precipitates. Consequently Fe concentration is increased in surface sediments and metal to Fe ratios may be changed (Finney and Huh, 1989). So using Fe as a normalization element can lead to an underestimation of metal inputs from anthropogenic sources. However, some metals such as As and Zn can bind to Fe precipitates (e.g., iron oxyhydroxides) and their concentrations may covary with Fe (Dolye and Otte, 1997), making iron a better normalization element for these metals. Enrichment of Fe near the surface was not found in sediment core samples collected from ST (Hwang et al., submitted for publication-b). Hornberger et al. (1999) also found no diagenetic

increase of Fe in surface layers of all cores collected from the various locations in SFB. One problem that may need attention especially for ST is the previous production of sulfuric acid that generated a large volume of cinder waste from the roasting of iron pyrite ore. A former chemical manufacturing company dumped large amounts of cinder waste on site so the Fe level in ST may have been affected. However, Fe concentrations measured in the ST sediments collected for this study were close to those found in reference marshes and the impact of previous cinder waste dumping on the levels of Fe may not be substantial. So, both diagenetic surface enrichment of Fe and cinder waste dumping do not likely hamper the use of Fe as a reference element for this study. Enrichment factors for the northern California marshes did not differ substantially using either Al or Fe. Using Fe as a reference element for CS makes it easier to compare with the Southern California Bight study (Schiff and Weisberg, 1999).

The enrichment factor (EF) of this study is defined as

$$EF = (C_M/C_R)_{\text{sample sediment}} / (C_M/C_R)_{\text{baseline sediment}}$$

where C_M is the concentration of metal (M) and C_R is the concentration of a reference metal (Al or Fe). The EFs of sedimentary metals in northern California marshes (ST, CC, TP, WC) and southern California marsh (CS) were calculated using the baseline concentrations reported by Hornberger et al. (1999) and Schiff and Weisberg (1999), respectively. Aluminum normalized concentrations of metals in ST sediments indicate that anthropogenic sources were predominant over natural input for Cu, Pb, Ag, and Zn. EFs revealed that Pb was the most anthropogenically impacted metal (Fig. 3). EFs for Pb in ST sediments varied from 8 to 49 (median = 15). Sediments from CC, TP, and WC also had high EFs for lead (2–8). Anthropogenic enrichment of metals was expected to be a minimum at these reference marshes because these marshes have been much less impacted by human activities. High lead enrichment in these marshes indicates that lead contamination is

ubiquitous, likely due to historic use of leaded gasoline that was atmospherically transported to remote areas. EFs of Ag in sediments from ST and CC were similar and fell within a range from 1 to 10 that is similar to a general pattern of the whole bay area (Hornberger et al., 1999). Atmospheric and fluvial sources of silver are considered relatively small in San Francisco Bay so, industrial and municipal effluents are likely the major sources (Squire et al., 2002). Cu and Zn were enriched only in sediments from ST. EFs varied from 1 to 5 and 2 to 7 for Cu and Zn, respectively (Fig. 3). No anthropogenic enrichment was found for Ag, Cu, and Zn in sediments from TP and WC.

Aqueous and sedimentary concentrations of Ni in SFB watershed have often exceeded the water and sediment quality guidelines (SFEI, 2005b) so anthropogenic input of Ni can be suspected. However, Ni in sediments from all study areas was similar to baselines and EFs were close to 1, indicating that sedimentary Ni measured in the present study is not likely of anthropogenic origin. Contrary to other metals such as Cu, Pb, and Zn, which have many anthropogenic sources, Ni has very limited anthropogenic sources. Oil refinery, steel mill, and wastewater treatment effluent are the major anthropogenic source of Ni (Brown and Luoma, 1995; Sedlak et al., 1997) so anthropogenic enrichment of Ni may occur rarely, especially in areas like ST where a large amount of wastewater effluent input is not expected. Ni in sediment cores collected from clean (Tomales Bay) and contaminated (SFB and ST) areas showed the same depth profile (no difference between surface and 200 cm), confirming that the majority of Ni has been coming from natural sources (Hornberger et al., 1999; Hwang et al., submitted for publication-b). Soils in watersheds flowing into SFB contain Ni-rich source rocks such as serpentinite, in which Ni concentrations reach up to $3000 \mu\text{g g}^{-1}$ (Topping and Kuwabara, 2003). Ni concentrations in average continental crust are only in the range of $20 \mu\text{g g}^{-1}$ (Taylor and McLennan, 1985). Cr and V in all northern California marshes were similar and did not show any enrichment compared to baseline concentrations.

As shown in Table 1, anthropogenically enriched metals (Ag, Cu, Pb, and Zn) with higher EFs had greater variation in their surface sediment concentrations. The coefficients of variation (percentage of standard deviation against mean) of these metals in ST were 77% (Zn), 68% (Pb), 59% (Cu), and 43% (Ag) while other metals (Ni, V, Cr, Li) that are dominated by natural inputs had much lower and constant coefficients of variation (23–27%), which are the same as those of Al (26%) and Fe (25%). EFs of As and Cd were not calculated because baseline concentrations were not available for these metals. As a less conservative approach, the high coefficient of variation of As (54%) and Cd (75%) indicate that these metals in ST sediments are likely enriched by anthropogenic input.

Sedimentary metals in CS had higher iron normalized enrichment factors for Ag, Cu, Pb, and Zn only at some stations (e.g., CS-A, CS-8) that are located in the head of main channels. The enrichment factors of these metals also

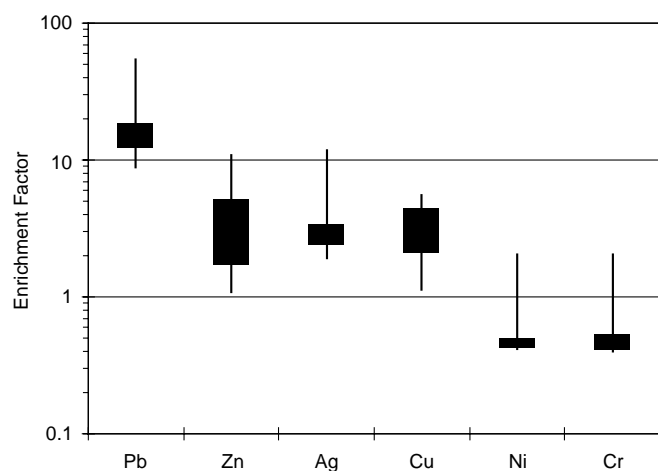


Fig. 3. Enrichment factors of metals in sediments from Stege Marsh, San Francisco Bay. Lines indicate the full range of the data and bars indicate the 25th and 75th percentiles.

gradually decreased towards the downstream ends of channels. As and Ni in sediments from all CS stations were close to the baseline levels that were found in southern California coastal shelf sediments. Schiff and Weisberg (1999) found that southern California coastal shelf sediments were anthropogenically enriched with these two metals only for a few samples (<2%). Regression results of As–Fe and Ni–Fe relationships in sediments from CS and the Southern California Bight are very similar. Coefficients of variation of Al (84%), Fe (76%), Ni (77%) and Li (68%) in CS sediments were relatively constant compared to anthropogenically impacted metals. Similarly to ST, coefficients of variation of highly anthropogenically impacted metals such as Ag (240%), Cu (115%), Pb (137%), and Zn (133%) in CS were much higher than other metals. As, Cd, Cr, and V also had low coefficients of variation (52–84%), indicating that these metals are less impacted by anthropogenic input. In the other marshes, the CVs of all metals are relatively constant (19–59%), consistent with their classification as reference marshes.

Acknowledgements

We would like to thank William Schilling and Marlene Relja for their help in laboratory chemical analyses. This research has been supported by a grant from the US Environmental Protection Agency's Science to Achieve Results (STAR) Estuarine and Great Lakes (EaGLE) Coastal Initiative through funding to the Pacific Estuarine Ecosystem Indicator Research (PEEIR) Consortium, US EPA Agreement #EPA/R-82867601. Research activities at Tomales Bay were conducted under National Marine Sanctuary Permit #GFNMS-2002-005. The research was also supported in part by funding from the University of California Toxic Substances Research and Teaching Program.

References

- Alpers, C.N., Hunerlach, M.P., 2000. Mercury contamination from historic gold mining in California. FS-061-00. United States Geological Survey, Sacramento, CA.
- Bay, S., Jones, B.H., Schiff, K., Washburn, L., 2003. Water quality impacts of stormwater discharges to Santa Monica Bay. *Mar. Environ. Res.* 56, 205–223.
- Brown, C.L., Luoma, S.N., 1995. Use of the euryhaline bivalve *Potamocorbula amurensis* as a biosentinel species to assess trace metal concentration in San Francisco Bay. *Mar. Ecol. Prog. Ser.* 124, 129–142.
- California Department of Transportation (Caltrans), 2003. A review of the contaminants and toxicity associated with particles in stormwater runoff. CTSW-RT-03-059.73.15, California Department of Transportation, Sacramento, CA.
- Callender, E., Rice, K.C., 2000. The urban environmental gradient: anthropogenic influences on the spatial and temporal distributions of lead and zinc in sediments. *Environ. Sci. Technol.* 34, 232–238.
- Cook, J.M., Gardner, M.J., Griffiths, A.H., Jessep, M.A., Ravenscroft, J.E., Yates, R., 1997. The comparability of sample digestion techniques for the determination of metals in sediments. *Mar. Poll. Bull.* 34, 637–644.
- Council, T.B., Duckenfield, K.U., Landa, E.R., Callender, E., 2004. Tire-wear particles as a source of zinc to the environment. *Environ. Sci. Technol.* 38, 4206–4214.
- Daskalakis, K.D., O'Connor, T.P., 1995. Normalization and elemental sediment contamination in the coastal United States. *Environ. Sci. Technol.* 29, 470–477.
- Davis, A.P., Shokouhian, M., Ni, S., 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere* 44, 997–1009.
- Dolye, M.O., Otte, M.L., 1997. Organism-induced accumulations of iron, zinc and arsenic in wetland soils. *Environ. Poll.* 96, 1–11.
- Dunlap, C.E., Bouse, R., Flegal, A.R., 2000. Past leaded gasoline emissions as a nonpoint source tracer in Riparian systems: a study of river inputs to San Francisco Bay. *Environ. Sci. Technol.* 34, 1211–1215.
- Finney, B., Huh, C., 1989. History of metal pollution in the Southern California Bight: an update. *Environ. Sci. Technol.* 23, 294–303.
- Flegal, A.R., Conaway, C.H., Scelfo, G.M., Hibdon, S.A., Sanudo-Wilhelmy, S.A., 2005. A review of factors influencing measurements of decadal variations in metal contamination in San Francisco Bay, California. *Ecotoxicology* 14, 645–660.
- Fostner, U., Wittman, G.T.W., 1983. *Metal Pollution in the Aquatic Environment*. Springer-Verlag, Berlin.
- Goals Project, 1999. Baylands ecosystem habitat goals: a report of habitat recommendation. United States Environmental Protection Agency/San Francisco Bay Regional Water Quality Control Board, Oakland, CA.
- Goals Project, 2000. Baylands ecosystem species and community profiles: life histories and environmental requirements of key plants, fish, and wildlife. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.
- Greenfield, B.K., Davis, J.A., Fairey, R., Roberts, C., Crane, D., Ichikawa, G., 2005. Seasonal, interannual, and long-term variation in sport fish contamination, San Francisco Bay. *Sci. Total. Environ.* 336, 25–43.
- Higashi, R.M., Cassel, T., Green, P.G., Fan, T.W.-M., 2005. ¹³C-tracer studies of soil humic substructures that reduce heavy metal leaching. In: Edgar, B., Tiffany, Z. (Eds.), *Subsurface Contamination Remediation: Accomplishments of the Environmental Management Science Program*, ACS Symposium Series 904.
- Hornberger, M.I., Luoma, S.N., van Green, A., Fuller, C., Anima, R., 1999. Historical trends of metals in the sediments of San Francisco Bay, California. *Mar. Chem.* 64, 39–55.
- Hwang, H.-M., Green, P.G., Young, T.M., in press. Tidal salt marsh sediment in California, USA. Part 1: Occurrence and sources of organic contaminants. *Chemosphere*, doi:10.1016/j.chemosphere.2005.12.024.
- Hwang, H.-M., Green, P.G., Young, T.M., submitted for publication-a. Tidal salt marsh sediment in California, USA. Part 3: Probability of toxic effects of organic contaminants and trace metals and their bioaccumulation in crab and fish. *Chemosphere*.
- Hwang, H.-M., Green, P.G., Young, T.M., submitted for publication-b. Tidal salt marsh sediment in California, USA. Part 4: Historical trends of organic contaminants and trace metals. *Chemosphere*.
- Luoma, S.N., 1990. Processes affecting metal concentrations in estuarine and coastal sediments. In: Furness, R., Rainbow, P. (Eds.), *Heavy Metals in the Marine Environment*. CRC Press, Boca Raton, FL, pp. 51–66.
- Makepeace, D.K., Smith, D.W., Stanley, S.J., 1995. Urban stormwater quality: summary of contaminant data. *Crit. Rev. Environ. Sci. Technol.* 25, 93–139.
- Mitsch, W.J., Gosselink, J.G., 2000. *Wetlands*, third ed. John Wiley and Sons, New York.
- Monroe, M.W., Kelly, J., 1992. San Francisco Bay Estuary Project, State of the Estuary: A report on the conditions and problems in the San Francisco Bay/Sacramento-San Joaquin Delta Estuary Project, Oakland, CA.

- Nriagu, J.O., 1994. Mercury pollution from the past mining of gold and silver in the Americas. *Sci. Total. Environ.* 149, 167–181.
- Office of Environmental Health Hazard Assessment (OEHHA), 1999. Overview of San Francisco Bay sport fish contamination and response activities. Office of Environmental Health Hazard Assessment, Oakland, CA.
- Peijnenburg, W.J.G.M., Jager, T., 2003. Monitoring approaches to assess bioaccessibility and bioavailability of metals: matrix issue. *Ecotoxicol. Environ. Safety* 56, 63–77.
- Rice, K.C., Conko, K.M., Hornberger, G.M., 2002. Anthropogenic source of arsenic and copper to sediments in a suburban lake, northern Virginia. *Environ. Sci. Technol.* 36, 4962–4967.
- San Francisco Bay Regional Water Quality Control Board (SFBRWQCB), 1998. Staff report: ambient concentrations of toxic chemicals in San Francisco Bay sediments. San Francisco Bay Regional Water Quality Control Board, Oakland, CA.
- San Francisco Estuary Institute (SFEI), 2005a. The pulse of the estuary: monitoring and managing water quality in the San Francisco Estuary. SFEI Contribution 78. San Francisco Estuary Institute, Oakland, CA.
- San Francisco Estuary Institute (SFEI), 2005b. The Regional Monitoring Program for trace substances in the San Francisco Estuary. 2003 Annual monitoring results. San Francisco Estuary Institute, Oakland, CA.
- Schiff, K.C., Weisberg, S.B., 1999. Iron as a reference element for determining trace metal enrichment in southern California coastal shelf sediments. *Mar. Environ. Res.* 48, 161–176.
- Sedlak, D.L., Phinney, J.T., Bedsworth, W.W., 1997. Strongly complexed Cu and Ni in wastewater effluents and surface runoff. *Environ. Sci. Technol.* 31, 3010–3016.
- Sogard, S.M., Able, K.W., 1991. A comparison of eelgrass, sea lettuce macroalgae, and marsh creeks as habitats for epibenthic fishes and decapods. *Estuar. Coast. Shelf Sci.* 33, 501–519.
- Squire, S., Scelfo, G.M., Revenaugh, J., Flegal, A.R., 2002. Decadal trends of silver and lead contamination in San Francisco Bay surface waters. *Environ. Sci. Technol.* 36, 2379–2386.
- Steding, D.J., Dunlap, C.E., Flegal, A.R., 2000. New isotopic evidence for chronic lead contamination in the San Francisco estuary system: implications for the persistence of past industrial lead emission in the biosphere. *Proc. Natl. Acad. Sci.* 97, 11181–11186.
- Taylor, S.R., McLennan, S.M., 1985. *The Continental Crust: Its Composition and Evolution*. Blackwell Scientific Publication, Oxford.
- Topping, B.R., Kuwabara, J.S., 2003. Dissolved nickel and benthic flux in South San Francisco Bay: a potential for natural sources to dominate. *Bull. Environ. Contam. Toxicol.* 71, 46–71.
- URS, 1999. University of California, Berkeley Richmond Field Station. Filed sampling and analysis plan and tiered risk evaluation. Prepared for University of California, Berkeley, URS Corporation, Oakland, CA.
- Weis, J.S., Weis, P., 2004. Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. *Environ. Int.* 30, 685–700.